Highly accurate wavefunctions for two-electron systems using two parameteres

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Abstract. It is shown for two electron atoms that ground-state wavefunctions of the form

$$\Psi(\vec{r_1}, \vec{r_2}) = \phi(\vec{r_1})\phi(\vec{r_2})(\cosh ar_1 + \cosh ar_2)(1 + 0.5r_{12}e^{-br_{12}})$$

where $\vec{r_1}$ and $\vec{r_2}$ are the coordinates of two electrons and $r_{12} = |\vec{r_1} - \vec{r_2}|$, can be made highly accurate by optimizing a, b and ϕ. This is done by solving a variationally derived equation for ϕ for a given a and b and finding a and b so that the expectation value of the Hamiltonian is minimum. For the set $\{a, b, \phi\}$ the values for various quantities obtained from the above wavefunction are compared with those given by 204-parameter wavefunction of Koga *et al* [11]and are found to be matching quite accurately(within ppm) with them.

1. Introduction

The simplest of many-electron systems are those with two electrons like ions of the helium isoelectronicc series or a harmonium atom. Since the Schrödinger equation for these systems cannot be solved analytically, accurate solutions are obtained by using the variational principle for the energy. Thus an approximate parametrized form of the wavefunction is chosen incorporating the effect of electron-electron interactionon in the wavefunction and the expectation value of the Hamiltonian (atomic units are used)

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + v_{ext}(\vec{r_1}) + v_{ext}(\vec{r_2}) + \frac{1}{r_{12}} \tag{1}$$

is minimized with respect to the parameters in the wavefunction. This leads to an optimized approximate wavefunction and the corresponding energy. The various forms used for the wavefunctions are those by Hylleraas[1, 2, 3, 4, 5], Chandrasekhar[6] and Kinoshita[7, 8]. As an example of how these forms incorporate the effect of electron-electron interaction, we consider the Chandrasekhar wavefunction for two-electron atom given as

$$\Psi_C(\vec{r_1}, \vec{r_2}) = C_N(e^{-ar_1}e^{-br_2} + e^{-ar_2}e^{-br_1}) \tag{2}$$

where a and b are the parameters to be optimized and C_N is the normalization constant. The idea behind writing the wavefunction in the form above is as follows. In the ground state of a two electron atom, each electron moves essentially in a hydrogen-atom like $1s$ orbital (of the form e^{-ar})but because of electron closer to nucleus, the effective nuclear charge is different for the outer electron. Hence the parameters for the orbitals of the two electrons are different. Symmetrization of the resulting

product wavefunction then leads to the form given in equation (2). Another way of obtaining accurate wavefunctions has been given by Hylleraas[1, 2, 3, 4, 5] where the wavefunction is expressed as

$$\Psi_H(\vec{r_1}, \vec{r_2}) = e^{-\zeta s} \sum_{i=1}^{N} c_i s^{l_i} t^{m_i} u^{n_i} \tag{3}$$

where $s = r_1 + r_2, \ t = r_1 - r_2, \ \ u = |\vec{r_1} - \vec{r_2}|$, and ζ and c_i are variational parameters. The most accurate calculation using this form of the wavefunction has been that of Frankowski and Pekeris[9], who used a 246-term wavefunction to get highly accurate energies for the helium isoelctronic series. Employing a 230-term wavefunction Freund et al. [10] got essentially the same results as those of [9]. Using another modification to Hylleraas type wavefunction, Koga *et al* [11] constructed a 204-term wavefunction that gives energy within 16 nano-Hartree of the energy given in [10]. In addition, usefulness of the work of [11] lies in the fact that they expressed the electronic density of the 204-parameter wavefunction in a simple analytical form with 43 parameters. Along similar lines, in 1994 Umrigar and Gonze[12] constructed very accurate densities for He isoelectronic series by using 491-term wave function having the same form of the basis set as used by Freund *et al* . The resulting densities have been used in the past to construct exchange-correlation potential[12] and to calculate[13] polarizability of two electron atoms and also to study derivative discontinuity of the exchange-correlation[14] of potential of density functional theory. Examples of references [12, 13, 14] are sufficient to show that the availability of accurate densities facilitate studies in fundamental aspects of density functional theory[15]. As such methods that can give accurate densities with relative ease are desirable to facilitates such studies. With this in mind Le Sech[16] introduced a semianalytical wavefunction for the ground state of two electron atoms and ions that gives energy within parts per million (ppm) of the answers of references [9, 10, 11].

2. Le Sech wavefunction

The wavefunction proposed by Le Sech is motivated by the intuitive aspects of the Chandrashekhar wavefunction and correlation factor given by earlier studies [17]. The wavefunction is given as

$$\Psi_L(\vec{r_1}, \vec{r_2}) = C_N e^{-Z(r_1 + r_2)} (\cosh a r_1 + \cosh a r_2)(1 + 0.5 r_{12} e^{-b r_{12}}) \tag{4}$$

where C_N is the normalization constant and Z is the atomic number of the atomic system. The factor $(\cosh a r_1 + \cosh a r_2)$ is chosen so that cusp condition[18] is satisfied exactly by the wavefunction. The parameters a and b are obtained variationally by minimizing the expectation value of the Hamiltonian with respect to them. The energies so obtained for H⁻, He, Li⁺, Be²⁺, B³⁺ are given in Table 1 along with the exact energies obtained in [11]. The differences between the two energies are also shown. We mention that the values of parameters a and b and the corresponding energies obtained by us are slightly different from those reported in ref [16]. It is clear from Table 1 that the wavefunction Ψ_L of Equation (4) leads to accurate energies with the difference from those of [11] becoming smaller with increasing Z. The difference for H⁻ is 1899 parts per million and goes down to 104(*ppm*)for B^{3+}. We note that the wavefunction of Equation (4) can be improved further with the inclusion of one more parameter and leads to a closer agreement with the exact energies.

Table 1. Energies for He-like systems using approximate wavefunction Ψ_L of Equation (4) and Ψ_{ML} of Equation (9). Their comparision with the energies given in [11](given in the column under Ψ_K) is also made in the table. The differences of each energy from that given in [11] is given in ppm under the energies.

Atom	Ψ_L			Ψ_K	Ψ_{ML}		
	a	b	-Energy(a.u.)	-Energy(a.u.)	-Energy(a.u.)	a	b
H⁻	0.58	0.06	0.5267 (1899)	0.5277	0.5271 (1137)	0.62	0.06
He	0.72	0.20	2.9020 (586)	2.9037	2.9028 (310)	0.93	0.20
Li⁺	0.87	0.36	7.2778 (289)	7.2799	7.2788 (151)	1.19	0.36
Be²⁺	0.99	0.52	13.6533 (161)	13.6555	13.6544 (81)	1.48	0.54
B³⁺	1.10	0.67	22.0286 (104)	22.0309	22.0297 (55)	1.72	0.70

The question we now ask is how accurate are the densities given by Ψ_L? This is important from the point of view of having an accurate and easily accesible density of two electron systems if we were to employ them to investigate the foundational aspects of density functional theory of many electron systems in general and two electron systems in particular. To this end we present in Table 2 the values of $\rho(r=0)$, $\frac{d\rho}{dr}|_{r=0}$ and in Table 3 and 4 various moments of the densities obtained from the Le Sech wavefunction. A comparision of the results is made with the accurate values of those obtained from the densities given in [11]. It is seen that the densities given by Ψ_L are smaller than the exact values of the densities at $r=0$. Since the Kato-cusp condition is satisfied by both Ψ_L and Ψ_K, the derivative $|\frac{d\rho}{dr}|_{r=0}$ are also small in comparision with the exact density. This implies that the Le Sech densities may be little more spread out than the exact densities. We also test the density in terms of

Table 2. Densities and its derivative at $r=0$ are calculated by using Ψ_L, Ψ_{ML}. For the density given by Koga *et al* (given in the column under ψ_K) we have used the exact expression given in their paper[11] to calculate $\rho(r=0)$ and $-\frac{d\rho}{dr}(r=0)$. We see that Le Sech density and its derivatives are smaller than the density given in[11] at $r=0$ but the Modified Le Sech density is close to them. Numbers given are in atomic units.

Atom	$\rho(r=0)$			$-\frac{d\rho}{dr}(r=0)$		
	Ψ_L	Ψ_K	Ψ_{ML}	Ψ_L	Ψ_K	Ψ_{ML}
H⁻	0.310	0.323	0.329	0.621	0.649	0.657
He	3.554	3.621	3.616	14.214	14.483	14.462
Li⁺	13.552	13.704	13.693	81.312	82.223	82.185
Be²⁺	34.180	34.396	34.384	273.438	275.167	275.077
B³⁺	69.164	69.517	69.501	691.640	695.165	695.011

it satisfying the ionization potential (IP) theorem in Kohn-Sham density functional theory. Furthermore, we also study the accuracy of the corresponding Kohn-Sham exchange-correlation potential. According to the IP theorem [19, 20] the highest oc-

Next in Table 3 and Table 4, we present various moments of the density obtained from Ψ_L of Equation (4) and compare them with their exact counterparts. It is seen that $\langle r^{-2} \rangle$ and $\langle r^{-1} \rangle$ for Ψ_L are less than those obtained from[11] the exact density. This is consistent with the density for Ψ_L being smaller than the exact one near the nucleus. For $\langle r \rangle$, $\langle r^2 \rangle$ and $\langle r^3 \rangle$ on the hand, it is observed that their values are larger than the exact moments for most of the cases (exception is for H⁻). This again shows that for Ψ_L, the density is more spread out in general.

Table 3. Comparision of moments calculated by using Ψ_L of Equation (4) and Ψ_{ML} of Equation (9) with the moments given in [11] for two electron atoms. The latter are given in column under Ψ_K. Numbers are given in atomic units.

Atom	$\langle r^{-2} \rangle$			$\langle r^{-1} \rangle$		
	Ψ_L	Ψ_K	Ψ_{ML}	Ψ_L	Ψ_K	Ψ_{ML}
H⁻	2.145	2.233	2.229	1.348	1.366	1.367
He	11.878	12.035	12.002	3.363	3.377	3.376
Li⁺	29.574	29.855	29.762	5.362	5.376	5.375
Be²⁺	55.301	55.680	55.485	7.367	7.376	7.376
B³⁺	88.900	89.507	89.146	9.366	9.375	9.375

Table 4. The caption is same as that of Table 3

Atom	$\langle r \rangle$			$\langle r^2 \rangle$			$\langle r^3 \rangle$		
	Ψ_L	Ψ_K	Ψ_{ML}	Ψ_L	Ψ_K	Ψ_{ML}	Ψ_L	Ψ_K	Ψ_{ML}
H⁻	5.331	5.420	5.422	22.000	23.830	23.859	125.030	152.000	152.366
He	1.863	1.859	1.859	2.402	2.387	2.386	3.996	3.936	3.934
Li⁺	1.148	1.146	1.145	0.898	0.893	0.892	0.895	0.883	0.882
Be²⁺	0.829	0.829	0.829	0.465	0.464	0.464	0.331	0.328	0.328
B³⁺	0.650	0.649	0.649	0.285	0.284	0.284	0.157	0.156	0.157

cupied orbital eigenenergy is equal to negative of the ionization potential of a many electron system. Accordingly for a Kohn-Sham system for a given ground-state density of two electron system, its eigenvalue should be equal to $I = -(E + \frac{Z^2}{2})$ where E is the energy of the two-electron system. To test the accuracy of the Le Sech densities, we construct the corresponding Kohn-Sham system using the Zhao-Parr[21] method, which is described briefly in the following.

For the orbitals of noninteracting system of electrons the kinetic energy T_s and ground state density $\rho(r)$ are given by

$$T_s = \sum_i \langle \phi_i(\mathbf{r})| -\frac{1}{2}\nabla^2 |\phi_i(\mathbf{r})\rangle, \quad \rho(r) = \sum_i |\phi_i(r)|^2 \tag{5}$$

For a given ground state density, the Kohn-Sham system is formed by minimizing $T_s + \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$ with respect to ϕ_i's with the constraint.

$$\int \int \frac{[\rho(\mathbf{r}) - \rho_0(\mathbf{r})][\rho(\mathbf{r}') - \rho_0(\mathbf{r}')]}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}d\mathbf{r}' = 0 \tag{6}$$

which is equivalent to $\rho(r) - \rho_0(r) = 0$, and $\int |\phi_i|^2 d\mathbf{r} = 1$. This leads to the equation

$$-\frac{1}{2}\nabla^2\phi_i(\mathbf{r}) + v_{ext}(r)\phi_i(\mathbf{r}) + v(r)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \tag{7}$$

where

$$v(r) = \lambda \int \frac{[\rho(\mathbf{r}') - \rho_0(\mathbf{r}')]}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \tag{8}$$

where λ and ϵ_i are the Lagrangian multipliers to enforce the two constraints above. Equation (7) is solved self-consistently using a Herman-Skillman[22] program modified suitably. Since at the solution point $\rho(r) = \rho_0(r)$, the value of λ should go to infinity such that $v(r)$ remains finite. In this paper we have performed all the calculations for $\lambda = 30000$. We point out that for two electron systems, the Kohn-Sham systems can also be found directly from the Laplacian of the density. We however, chose Zhao-Parr method because it is more general and more accurate.
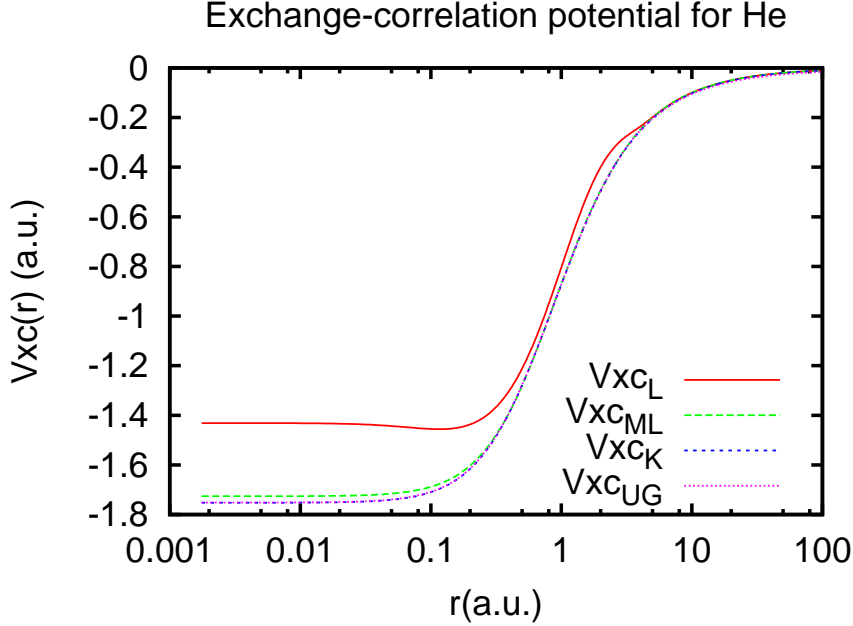
Table 5. Highest occupied orbital eigenvalue ϵ_{max} and ionization potential $I = -(E + \frac{Z^2}{2})$ for two electron systems. Numbers given are in atomic units

Atom	Ψ_L		Ψ_{ML}		I_{expt}[23]
	$-\epsilon_{max}$	I	$-\epsilon_{max}$	I	
H⁻	0.0613	0.0267	0.0276	0.0271	0.0277
He	0.8265	0.9020	0.9059	0.9027	0.9036
Li⁺	2.5718	2.7778	2.7821	2.7787	2.7798
Be²⁺	5.3581	5.6533	5.6593	5.6543	5.6557
B³⁺	9.1406	9.5286	9.5349	9.5296	9.5320

Shown in Table 5 are the values of $-\epsilon_{max}$ and I for Ψ_L for the ions studied in this paper. It is seen for Ψ_L that the values of ϵ_{max} and I are comparable to each other. However, they are not close enough to satisfy the IP theorem. Furthermore, the values of I are close to the experimental ionization potential, which shows that the total energies E for Ψ_L is accurate. On the other hand $-\epsilon_{max}$ is not accurate for Ψ_L. This is particularily evident for the densities of the H^- ion and He atom where the difference between the two is 121 and 8, percent respectively. Since the eigenvalue ϵ_{max} is determined by the asymptotic decay of the electron density, it is evident that asymptotically, the density given by Le Sech wavefunction is not accurate. This is further evidenced by the corresponding Kohn-Sham exchange-correlation shown in figure 1 where we have plotted the exchange-correlation potential of He for both Le Sech density as well as the density given in[11] and another accurate density of Umrigar and Gonze[12]. It is clear that Le Sech density leads to smaller magnitude of the exchange-correlation potential near the nucleus, which in turn gives densities which are more spread out.

It is evident from the results presented so for that the Le Sech wavefunction needs to be improved if it were to give accurate densities. The rest of the paper is then devoted to modifying the Le Sech wavefunction so that it leads to densities that can be employed to study exact properties in density functional theory.

Exchange-correlation potential for He

3. Modified Le Sech wavefunction

In this section we modify the Le Sech wavefunction so that the new wavefunction gives accurate energies as well as densities. We first point out how the Le Sech wavefunction can be made better. We feel that keeping the parameter Z (of the e^{-Zr} factor) fixed in the Le Sech wavefunction does not provide enough flexibility in the wavefunction and it is this component of the wavefunction that needs to be calculated more accurately. Hence the modified Le Sech (ML) wavefunction for the ground state of two electron atoms that we propose is

$$\Psi_{ML}(\vec{r_1}, \vec{r_2}) = \phi(r_1)\phi(r_2)(\cosh ar_1 + \cosh ar_2)(1 + 0.5r_{12}e^{-br_{12}}) \quad (9)$$

where for a given set of a and b, the orbital $\phi(r)$ is to be calculated self-consistently by solving the equation derived below which is obtained from the Euler equation

$$\frac{\delta}{\delta\phi(r)}[\langle H \rangle_{ML} - E\langle \Psi_{ML}|\Psi_{ML}\rangle] = 0 \quad (10)$$

where $\langle H \rangle_{ML}$ is the expectation value of the Hamiltonian of equation (2) with respect to the wavefunction Ψ_{ML} above. Equation (10) leads to following Schrödinger-like equation for $\phi(r)$ (in the equation below $r_{12} = |\vec{r} - \vec{r_2}|$, ∇ is gradient operater in terms of $\vec{r}$ and ∇_2 in terms of $\vec{r_2}$).

$$-\frac{1}{2}\nabla^2\phi(\mathbf{r}) - \frac{1}{A(r)}\nabla\phi(\mathbf{r}) \cdot \int f(r, r_2, r_{12})|\phi(r_2)|^2\nabla f(r, r_2, r_{12})d\mathbf{r_2}$$

$$-\frac{1}{2A(r)}\int[|\phi(r_2)|^2f(r,r_2,r_{12})\nabla^2f(r,r_2,r_{12})+|\phi(r_2)|^2f(r,r_2,r_{12})\nabla_2^2f(r,r_2,r_{12})$$

$$+|f(r,r_2,r_{12})|^2\phi(r_2)\nabla_2^2\phi(r_2)+2f(r,r_2,r_{12})\phi(r_2)\nabla_2\phi(r_2)\cdot\nabla_2f(r,r_2,r_{12})]d\mathbf{r_2}\phi(\mathbf{r})$$

$$-\frac{Z}{r}\phi(\mathbf{r})-\frac{Z}{A(r)}\int\frac{|\phi(r_2)f(r,r_2,r_{12})|^2}{r_2}d\mathbf{r_2}\phi(\mathbf{r})$$

$$+\frac{1}{A(r)}\int\frac{|\phi(r_2)f(r,r_2,r_{12})|^2}{|\mathbf{r}-\mathbf{r_2}|}d\mathbf{r_2}\phi(\mathbf{r})=E\phi(\mathbf{r}) \tag{11}$$

where

$$f(r,r_2,r_{12})=(\cosh ar+\cosh ar_2)(1+0.5r_{12}e^{-br_{12}}) \tag{12}$$

and

$$A(r)=\int|\phi(r_2)f(r,r_2,r_{12})|^2d\mathbf{r_2} \tag{13}$$

The equation above is solved self-consistently for a range of parameters a and b. The solution gives $\phi(r)$ and the corresponding energy E as the eigenvalue. The best wavefuncion corresponds to the values of a and b that give the minimum value of E.

We wish to point out that after completing our work, we discovered that the above equation was solved[24] in 1937 to obtain ground state energy and polarizability of the He atom. However the scope of the present paper is much wider. In this paper we investigate the wavefunction not only for the energy but also for the density it gives rise to. We present the results obtained by solving Equation (11) for the two electron atomic systems studied so for and show the accuracy of the energy as well as the density that is achieved by self-consistently determined Ψ_{ML}. From the results presented below, it becomes clear that Equation (11) provides a computationally straightforward method of obtaining highly accurate wavefunctions for two-electron systems. The method can also be applied with equal ease to other two-electrons systems such as electrons in a confined environment or harmonic oscillator potential.

Given in Table 1 are the results for the total energies of the modified Le Sech wavefunction Ψ_{ML} of Equation (9). As is evident, for the modified wavefunction, the total energies are better than those for the Le Sech functions. The modified wavefuction reduces the error of energies from Le Sech wavefunction by roughly a factor of 2. This is because the wavefunctions has been made more flexible. In addition to giving improved energies, Ψ_{ML} also gives much better densities than Ψ_L. We present these results in the following.

In Table 2, we also present the density and its derivative at $r=0$ obtained from Ψ_{ML} of Equation (9). We see that the values of modified Le Sech density and its derivative are very close the values obtained using exact expression given in [11]. In Table 3 and Table 4 we present the various moments of the density obtained by Ψ_{ML}. These moments are compared with the moments given in [11]. We get all the moments calculated by the modified Le Sech density close to the moments given in [11]. This implies that the modified Le Sech density is very close to the exact density.

In Table 5, IP theorem is tested for both Le Sech and modified Le Sech density, where the ϵ_{max} are calculated by solving Equation (7). We see that the modified Le Sech density satifies the IP theorem almost exactly. Finallly in Figure 1 we show

the exchange-correlation potential by using Le Sech density, modified Le Sech density, density given in[11] and for the density obtained by Umrigar and Gonze[12]. We see that the exchange-correlation potential given by modified Le Sech densities is very close to the exact potential.

4. Conclusion

Le Sech wavefunction[16], which gives very accurate energies for He-like systems, has been modified so that both the energies and densities obtained from the modified wavefunction are highly accurate. The densities so obtained can be used with confidence to perform fundamental density functional theory investigations. Along this line of investigation we are now employing the method proposed to study adiabatic connection in density functional theory.

Acknowledgments

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